DOE Chemical Hydrogen Storage Center of Excellence

Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides

Project ID# ST6

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Project Overview

Timeline

- Start: March 1, 2005
- End: February 28, 2010
- 20% complete

Barriers

- High cost and energy requirements for regenerating spent fuel from irreversible chemical H₂ storage systems
- Lack of understanding of cost and environmental impact of regeneration process

	Budget							
	FY05 Actual	FY06	FY07	FY08	FY09	Total		
DOE	\$229K	\$250K	\$353K	\$370K	\$389K	\$1,591K		
ROH	\$103K	\$112K	\$176K	\$168K	\$168K	\$727K		
Overall 69:31 DOE:ROH Split								





Objectives

Overall	 Define and evaluate novel chemistries and processes to produce chemical hydrogen storage materials to meet DOE 2010 targets, and with potential to meet 2015 targets Focus on Tier 1 Research: energy efficient and cost-effective options for B-OH to B-H conversion Leverage expertise and experience across Center Tiers 1, 2, 3: engineering requirements, economics, life cycle analysis Support DOE Chemical H₂ Storage Systems Analysis Sub-Group
FY05	Define goals/strategies, boundaries/assumptions; establish performance criteria/metrics
FY06	 Identify chemical pathways and process options Complete computational analysis of SBH regeneration routes (chemical and electrochemical) Develop experimental program Provide engineering support to H₂ Storage Systems Analysis program



Approach: Engineering-Guided R&D

Potential Regeneration Chemistries

Identify chemical routes

Compile & organize concepts

Define basic reaction envelopes & regeneration efficiency

Perform preliminary technical & economic viability analysis

Establish experimental & computational needs

Define leading options

Viable Regeneration Chemistries and Process Options

Engineering Assessment Reduces Technical Risk



Accomplishments

- Established performance-based metrics
- Identified potential regeneration routes
 - Metal reduction of borate
 - Electroreduction of borate
 - Borane-based routes
- Established framework for Analysis
 - Life Cycle Inventory
- Ammonia borane
 - Conducted preliminary cost and thermal stability assessments



Accomplishments: Performance-Based Metrics

				Baseline Cases		Performance of Option			
	CRITERIA		Criticality	Compressed H2 (700 bar)	Liquid H2	Brown-Schlesinger Process	Metal Reduction	Electrochemical	Borane-Based
Ī	0	Safety Score (Risk Analysis)	Paramount						
	1 H2 weight density meets 2010 DOE requirements (2 kWh/kg or 6 wt%)		Must						
		H2 weight density meets 2015 DOE requirements (3 kWh/kg or 9 wt%)	Desirable					•	
	2	H2 volume density meets DOE 2010 requirements (1.5 kWh/L or 0.045 kg/L)	Must				Optio	ons Gene	rated
		H2 volume density meets 2015 DOE requirements (2.7 kWh/L or 0.081 kg/L)	Desirable						
	3	Storage system cost meets DOE targets: 2010 = \$4/kWh (\$133/kg H2) 2015 = \$2/kWh (\$67/kg)	Must						
	4	Operating Ambient Temp. (DOE targets): 2010 = -30/50 (sun) °C 2015 = -40/60 (sun) °C	Must						
	5	Loss of Useable Hydrogen (DOE targets): 2010 = 0.1 [(g/h)/kg H2 stored] 2015 = 0.05 [(g/h)/kg H2 stored]	Must		Key Metrics for Selection of			tion of	
	6	Fuel cost meets DOE requirements: \$2-\$3/ gal gasoline equivalent	Must			Regeneration Process: • Fuel cost \$2 - \$3 gal gasoline equivalent • Ideal thermodynamic efficiency based on "burn ratio" of >60% • Measured energy efficiency of 60%			
	7a	High energy efficiency: Ideal thermo. efficiency based on 'burn ratio' of > 60%	Desirable		- Fuel a				
	712	High energy efficiency: Measured onergy efficiency of 60%	Desirable						rn
	8	Low capital cost (complexity, # UOps, technical risk)	Optional						
	9	Low operating cost	Optional		• Meas				
	10	Low raw material (RM) cost	Optional						
	11	No Path, Clear Path, or Demonstrated	Optional						
Ī	12	Logistics (availability of RM's)	Optional						
Ī	13	Low EHS risk	Optional						
	RESULT								



Accomplishments: Identification of NaBH₄ Regeneration Chemistries

- Metal reduction of borate
- Electrochemistry
- Borane-based routes
- Elemental synthesis
- Metathesis reactions
- Transfer hydrogenation

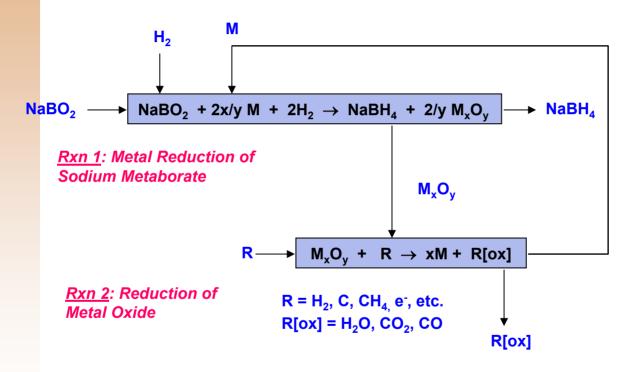
Construct overall reaction pathway



- Theoretical energy efficiency
- Reductant regeneration requirements
- Energy costs
- Raw material cost and availability



Accomplishments: General Pathway for Metal Reduction of Borate



Fast-fail Metrics

- Energetics of both reaction steps
- Metal reductant regeneration requirements
- Energy costs
- Raw material cost and availability

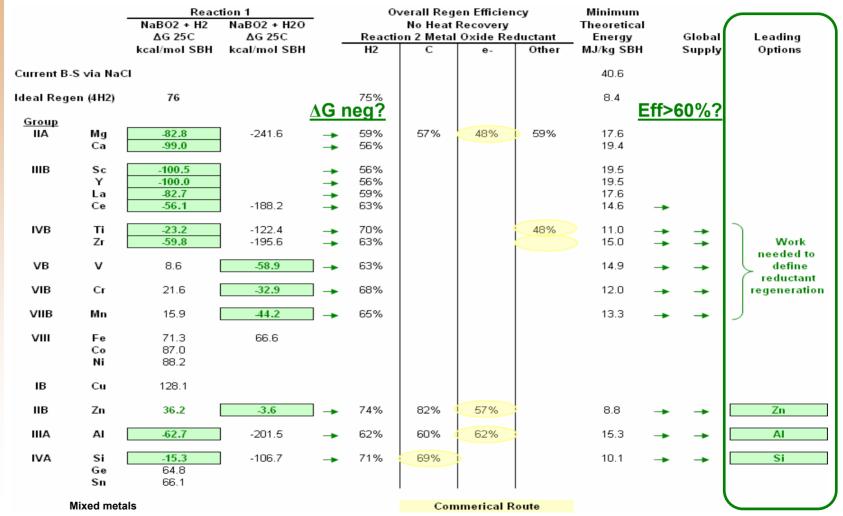
Net: $NaBO_2 + 2H_2 + R \rightarrow NaBH_4 + R[ox]$



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% Regen Eff = Usable Energy Released / Total Energy Used* = 100 * \Delta G_{cmb} H<sub>2</sub> prod / (\Delta G_{cmb} reductant + \Delta G_{rxn} NaBO<sub>2</sub>\rightarrow NaBH<sub>4</sub>) = 75% ideal
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^{*} Described at DOE H₂ Storage Engineering Analysis meetings, Argonne National Lab (10/12/05) and Palm Springs (11/18/05)

Accomplishments: Leading Metal Systems Identified





Accomplishments: Electrolytic Reduction of B-OH to B-H

- Collaboration with Penn State, LANL, MCEL
 - Validated analytical methods and electrolytic cell
 - Established reporting criteria and metrics
 - Previous Rohm and Haas successes shared with Team
 - Concepts suggested for improvement
 - Guide experimental activities
 - Testing at Penn State University
- Two electrolytic process routes identified
 - Laboratory evaluations
 - · Boron substrate: borate, alkyl borates, alkoxyborohydrides
 - Solvent systems: aqueous, non-aqueous
 - Cathode materials: hydrophobic composites, high hydrogen overpotential systems, gas diffusion cathodes
 - 1-step direct conversion to NaBH₄
 - 2-step conversion through NaBH(OCH₃)₃



Accomplishments: Positive Results for One-Step Electroreduction

Cathode Material	Catholyte	Current Density, mAmps/cm²	Current Efficiency
Teflon / Ni flag	0.5M boric acid 1M TMAH	50	2.9%
LaNi ₅ flag	10M NaOH 0.5M boric acid 1% TMAH	20 – 65	0.1%
Nickel / carbon gas diffusion electrode	10M NaOH 0.5M boric acid 1% TMAH	150	0.15%

- Advanced cathode materials (hydrophobic cathodes, high surface area cathodes)
- High current densities
- Alkylammonium salts and other means to minimize water electrolysis and favor borate reduction
- Analytical method : RDE voltammetry, detection limit ~50μM NaBH₄
- Typical operating parameters
 - Membrane divided Astris acrylic resin test cell
 - Nafion® 324 membrane
 - Anode : Pt or Pt-clad niobium
 - 1M NaOH anolyte



Accomplishments: Positive Results for Two-Step Electroreduction

Overall Process

- Trialkylborate → trialkoxyborohydride → borohydride
- B(OCH₃)₃ → NaBH(OCH₃)₃ → NaBH₄
- Competing disproportionation reaction: NaB(OCH₃)₄

Embodiments

- H₂ gas feed
- Nonaqueous solvents
- Regenerable redox species at cathode

Positive confirmation by ¹¹B NMR

- Conversion of B(OCH₃)₃ to NaBH(OCH₃)₃
- Conversion of NaBH(OCH₃)₃ to NaBH₄ (current efficiencies 15 47%)



Accomplishments: Borane-Based Pathways

- Demonstrated chemistry to form NaBH₄
 - NaH + $\frac{1}{2}$ B₂H₆ → NaBH₄
 - 2/3 Na₂CO₃ + 2/3 B₂H₆ \rightarrow NaBH₄ + 1/3 NaBO₂ + 2/3 CO₂
- Low cost, energy efficient method needed for B₂H₆ (or BH₃) generation
- Current industrial routes are inadequate
 - $3/2 \text{ NaBH}_4 + 2BF_3 \rightarrow B_2H_6 + 3/2 \text{ NaBF}_4$
 - 2NaBH₄ + H₂SO₄ → B₂H₆ + 2H₂ + Na₂SO₄



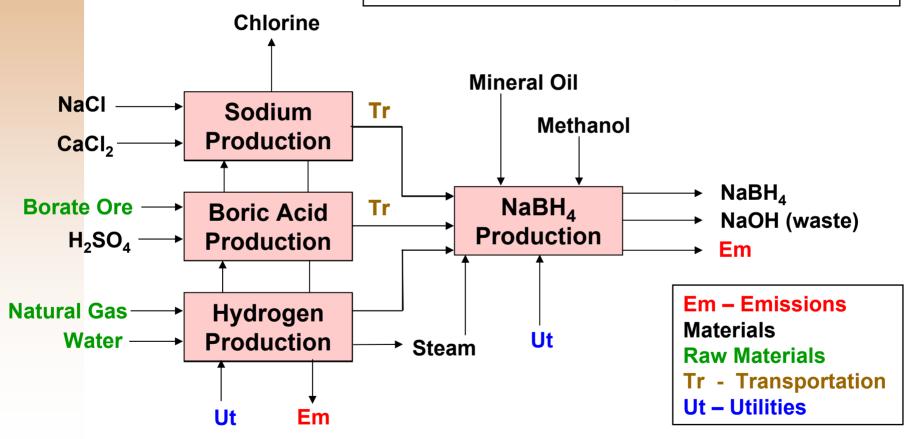
Accomplishments: Alternate Diborane Pathways

Path	Reaction	
1. Disproportionation	$6BX_3 + 6H_2 \rightarrow 6HBX_2 + 6HX$ $6HBX_2 \rightarrow \mathbf{B_2H_6} + 4BX_3$ <u>Net</u> : $2BX_3 + 6H_2 \rightarrow \mathbf{B_2H_6} + 6HX$	(X=F, Cl, Br)
2. Hydrogenolysis (Hyd)	$2B(OR)_3 + 6H_2 \rightarrow B_2H_6 + 6ROH$	$(R=H, C_1-C_4)$
3. Hyd via Red Metal	$2B(OR)_3 + 2AI + 3H_2 \rightarrow B_2H_6 + 2AI(OR)_3$	(other electro- positive metals)
4. Boron alkyl reduction	$2B(OR)_3 + 2AIEt_3 \rightarrow 2BEt_3 + 2AI(OR)_3$ $2BEt_3 + 6H_2 \rightarrow \mathbf{B_2H_6} + 6EtH$	
5. Amine borane I	2B(OH) ₃ + 6RNCO → 2B(NHR) ₃ + 6CO ₂ 2B(NHR) ₃ + 6CO → $\mathbf{B_2H_6}$ + 6RNCO Net: 2B(OH) ₃ + 6CO → $\mathbf{B_2H_6}$ + 6CO ₂	$(R=H, C_1-C_4)$
6. Amine borane II	$2B(OH)_3 + RNH_2 \rightarrow 2B(NHR)_3 + 6H_2O$ $2B(NHR)_3 + 6H_2 \rightarrow \mathbf{B_2H_6} + 6RNH_2$ \underline{Net} : $2B(OH)_3 + 6H_2 \rightarrow \mathbf{B_2H_6} + 6H_2O$	(R=H, C ₁ -C ₄)
7. Carbon	$B_2O_3 + 3C + 3H_2 \rightarrow B_2H_6 + 3CO$	
8. Elemental	$2B + 3H_2 \rightarrow B_2H_6$	



Accomplishments: Analysis

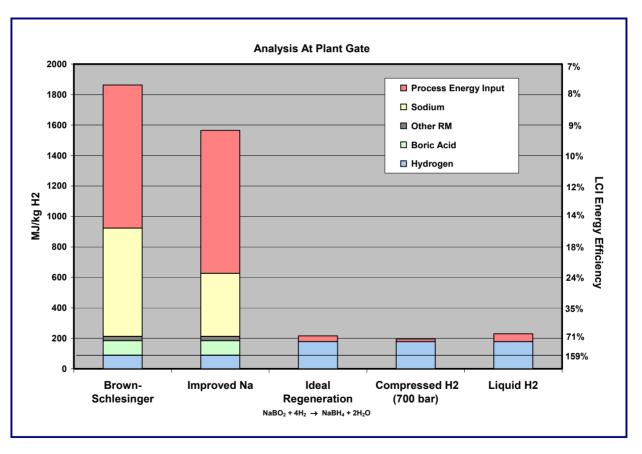
Life Cycle Inventory (LCI) Established for NaBH₄ via Current Brown-Schlesinger Process





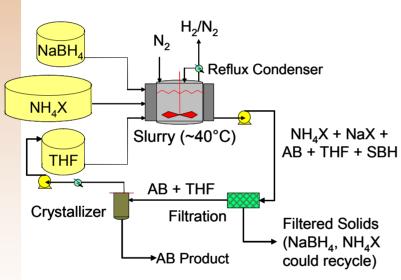
Accomplishments: Analysis

Comparison of LCI Gross Energy for H₂ at Regeneration Plant Fenceline





Accomplishments: Ammonia Borane Preliminary Cost Assessment



Hu et al. J. Inorg. Nucl. Chem. 1977, 39, 2147-2150.

- Current cost of ammonia borane is very high because it is priced as a specialty chemical. Low cost AB is needed to meet 2010 system cost targets.
- Initial fill chemistry will require NaBH₄
 NH₄+ salt route:

NaBH₄ + 1/n (NH₄)_nX
$$\rightarrow$$
 NH₃BH₃ + 1/n Na_nX + H₂

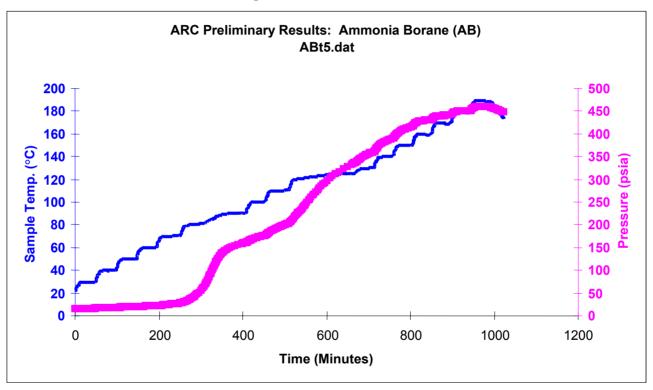
Diborane route:

$$\frac{1}{2}$$
 B₂H₆ + NH₃ \rightarrow NH₃BH₃
B₂H₆ from NaBH₄)

 AB regeneration should not involve NaBH₄ to meet regeneration fuel cost targets



Accomplishments: Ammonia Borane Thermal Stability



- DOE Stability Targets
 - 2010: <0.01% H₂ loss/hr at 50°C
 - 2015: <0.005% H₂ loss/hr at 60°C
- PNNL DSC and TGA data; no adiabatic stability data
- Rohm and Haas advanced calorimetry capabilities
 - ARC (accelerated rate calorimeter)
 - Uses small samples to test system stability under a wide range of conditions



Future Work

NaBH₄ Regeneration Routes

- Complete compilation of other chemical routes and conduct computational analysis to identify at least one option for laboratory demonstration (12/31/06)
- Laboratory demonstration of at least one process with overall efficiency
 ≥ 80% of theoretical (6/30/07)
- Develop conceptual design for laboratory demonstrated regeneration process and associated on-board system (9/30/07)
- Go/no go decision for NaBH₄ (9/30/07)

Ammonia Borane

- Develop conceptual AB manufacturing process and cost estimate
- Complete reaction calorimetry studies
 - Determine stability as function of time and temperature (50°C and 60°C)
 - Determine impact of aging and impurities on stability

Leverage ROH competencies

- Across Center
- Support DOE Chemical H₂ Storage Systems Analysis Sub-Group



Summary

NaBH₄ Regeneration Routes

- Leading metal reduction systems with lower energy usage have been identified
- Potential electroreduction routes identified
- Completing data-mining of other regeneration options
- Building efficient conceptual processes around them
- Estimate manufacturing cost

LCI

- Methodology developed for current Brown-Schlesinger process
- Build LCI models for regeneration alternatives
- Interface with H2A analysis tool

Ammonia Borane

- Lower cost NaBH₄ required
- ROH ARC stability data complements PNNL research



Publications and Presentations

F. Lipiecki, "Sodium Borohydride Regeneration and Analysis," Presentation to FreedomCAR Hydrogen Storage Tech Team, Houston, TX, Feb. 16, 2006



Critical Assumptions and Issues

Intellectual Property

- Agreements to cover jointly invented IP are critical, but difficult to establish with large number of Center partners
- Lack of agreements can inhibit collaboration and coinvention
- Separate IP agreements, involving fewer parties, therefore established for each sub-project (i.e., electrochemistry, engineering, etc.)

